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Preparation of Alumina Nanoparticle Suspensions with Narrow Particle Size Distribution

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Abstract—Dynamic light scattering (DLS) was applied to the study of the process of the preparing deaggregated water suspensions of alumina nanopowders with specific surface areas of 20–140 m^2/g. Nanopowders were prepared by the electric explosion of wire and laser evaporation and, according to electron microscopy (TEM), consisted of nonagglomerated spherical nanoparticles with lognormal size distribution. According to DLS, nonsedimenting water suspensions of alumina nanoparticles, stabilized by sodium citrate at a 5 mM concentration, contain substantial fraction of aggregates. The dynamics of the change in the mean average size of aggregates under exhaustive ultrasound treatment of suspensions with 10 g/l concentration for 1.5–4 h by two types of ultrasonic processors was studied. It was shown that the mean average size of aggregates exponentially diminishes by 1.5–2 times and the fraction of individual particles in suspension enlarges from 45 to 85%. Sequentially centrifuging the suspension at 18000 g separates the remaining aggregates and results in suspensions of individual alumina nanoparticles. Particle size distributions in these suspensions obtained by TEM and DLS are the same within experimental error.

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INTRODUCTION

The interface of any phase is characterized by an excess of free energy, which causes the spontaneous reduction of the interface. In the case of solid powders dispersed in a gaseous or liquid medium, it is expressed in individual particles sticking together, leading to an enlargement in size and a reduction in the contact area with the medium. The two terms "agglomeration" and "aggregation" are used to characterize this process. Sometimes these terms are used interchangeably, but more often they are used in a different sense, characterizing the stability of the emerging links between the primary particles. Unfortunately, at present, both in the Russian and foreign literature there are no generally accepted definitions that distinguish between these concepts. To be specific, hereinafter under "agglomerate" we will mean a stable formation: individual particles which are chemically bonded to each other and cannot be separated by mechanical action without the destruction of the particles themselves. In the "aggregation," primary particles are bounded by weaker van der Waals forces, which in principle can be disrupted while preserving the integrity of the particles.

Agglomeration is often observed during the formation of primary particles when the growing nuclei of the solid phase are in direct contact, whereby the growth of individual particles is combined with their mutual invasion, followed by the formation of a single crystal lattice in points of contact. The agglomeration of the primary particles can be readily detected in elec-

Table 1. Characteristics of nanopowders

No.	Identification number	S_{sp}, m^2/g	Phase composition	Acquisition technique, manufacturer
1	Al_2O_3-2212	139	100% γ	LEC, Institute of Electrophysics, Ural Branch, Russian Academy of Sciences
2	Al_2O_3-140ns	39.4	10% γ, 90% δ	EEW, Institute of Electrophysics, Ural Branch, Russian Academy of Sciences
3	Al_2O_3-117nfs	20.7	15% γ, 85% δ	EEW, Institute of Electrophysics, Ural Branch, Russian Academy of Sciences

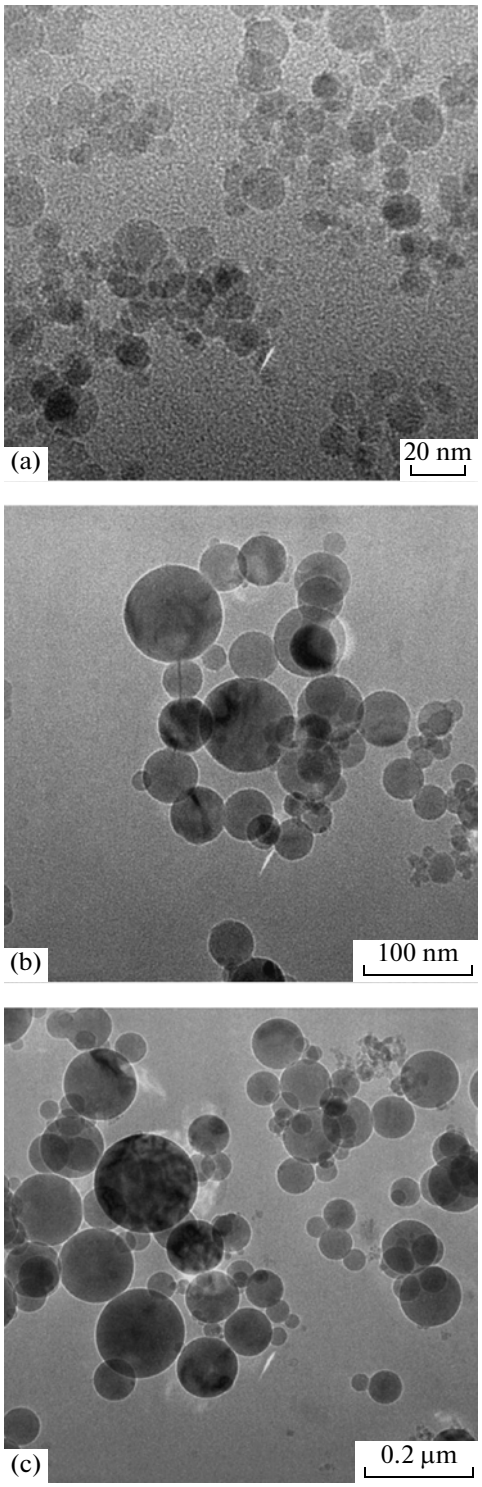


Fig. 1. Electron micrographs of nanopowders: (a) Al_2O_3-2212, (b) Al_2O_3-140ns, and (c) Al_2O_3-117nfs.

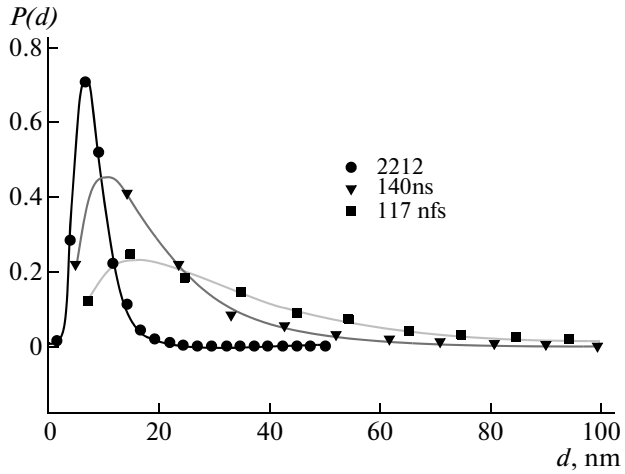


Fig. 2. Size distribution of particles in dry Al_2O_3 nanopowders.

tron micrographs using the absence of boundaries between individual particles.

The process of aggregation is formed between particles which have been formed and finished growing. Boundaries of aggregates between individual particles are clearly visible in electron micrographs. Aggregates are less stable formations than agglomerates. Particles in aggregates are bounded by physical forces, which, however, may reach quite high values, providing resistance to thermal motion.

Preventing the agglomeration of nanoparticles during their growth is one of the major technological problems in creating powdered nanomaterials. In some cases, this problem can be solved successfully in conjunction with high performance. Thus, in particular, methods for producing spherical nanoparticles by high energy physical dispersion in a gaseous medium have been developed at the Institute of Electrophysics, Ural Branch, Russian Academy of Sciences. We can make up to 500 g per hour of nonagglomerated nanopowder metal or its oxide with an average particle size of 10–100 nm, depending on the parameters of dispersing and gas medium using the dispersing electric explosion of metal wire (EEW). The method of laser evaporation and condensation (LEC), which at the same time allows the acquisition of nonagglomerated nanopowders with a narrow size distribution, have less performance.

However, in the process of receiving, collecting, storing, and using nanopowders, individual nanoparticles inevitably contact each other, whereby they spontaneously form aggregates. The destruction of aggregates (disaggregation) is a separate problem.

The processes of aggregation in aqueous suspensions by dispersing air-dry Al_2O_3 nanopowders produced by plasmochemical and electroexplosive methods have been studied in earlier work [1]. It is shown [1] that the primary aggregates in an amount of 35–50% (wt.) are stable; i.e., their further consolidation is not observed for quite a long time. The pH variation of the system was held, and it was found that the highest degree of aggregation is observed near the pI of the suspension. It has been noticed that it is very difficult

Table 2. Parameters of the lognormal distribution of particle sizes for dry Al_2O_3 nanopowders

No.	Identification-number	d_0, nm	σ	d_{av}^{*}, nm	d_{sur}^{2*}, nm	d_{wt}^{3*}, nm	d_{sc}^{4*}, nm	d_{BET}^{5*}, nm
1	Al_2O_3-2212	7.55	0.391	8.15	11.1	12.9	17.4	12.3
2	Al_2O_3-140ns	16.2	0.660	20.2	43.0	57.0	84.6	43.5
3	Al_2O_3-117nfs	28.2	0.736	36.7	85.7	110	144	82.8

* Average (arithmetic mean) value of the diameter of the particles in the sample.
[2]* Value of the diameter averaged over the surface of the particles.
[3]* Weighted average value of the diameter of the sample.
[4]* Value of the diameter, averaged by the intensity of scattering light.
[5]* Average value calculated from the specific surface.

to create a suspension of isolated nanoparticles and to get rid of the aggregates, even in the face of effective electrostatic stabilization. In this regard, the present work is devoted to experimental investigation of the laws of disaggregation and redispersion of Al_2O_3 alumina nanopowders obtained by methods of high-energy dispersion in the gas phase.

EXPERIMENTAL

Al_2O_3 nanopowders were obtained by the electrical explosion of wire and laser ablation [2].

The specific surface area of powders was determined by BET using a Micromeritics TriStar 3000 automated adsorption device. The phase composition was characterized by X-ray analysis with a Bruker D8 DISCOVER diffractometer using copper radiation with a graphite monochromator on the diffracted beam. Micrographs of the powders were obtained using a JEOL JEM 2100 TEM electron microscope. The characteristics of investigated powders are shown in Table 1.

Suspensions of nanoparticles with a concentration of 10 g/L were prepared by ultrasonic treatment (UST) in distilled water with the addition of 5 mM sodium citrate stabilizer with a Sonopuls HD 3200 submersible ultrasonic disperser (power 160 W) and a UZV-13/150-TN ultrasonic bath (power 240 W). The sizes of the particles in aqueous suspensions were measured by dynamic light scattering (DLS) on a Brookhaven ZetaPlus analyzer. Centrifuging of nanopowders suspensions after RCD was conducted by means of a Hermle Z383 centrifuge with a centrifugal acceleration on the order of 18000 g. All measurements were for suspensions carried out under isothermal conditions at 298 K.

RESULTS AND DISCUSSION

The alumina nanopowders investigated in this work are nonsintered and have a spherical shape (Fig. 1), which allows us to build the curves of particle size distribution (Fig. 2) by the optical analysis of photomicrographs.

All curves have a log-normal distribution of species, which is typical for dispersed materials obtained by grinding and crushing [3]:

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} e^{-\frac{(\ln d/d_0)^2}{2\sigma^2}},$$

where d_0 is the most probable value of the diameter and σ is the variance of distribution.

The parameters d_0 and σ of lognormal distributions for the nanopowders are shown in Table 2.

Figure 2 shows that the particle size distribution for the finest Al_2O_3-2212 nanopowder obtained by LEC is sufficiently narrow and fully fits into the range of 5 to 40 nm.

Parameters for the investigated nanopowders calculated on the basis of the average values of distribution are shown in Table 2. It is seen that different average sizes (distribution moments) are sufficiently close for finely nanopowder Al_2O_3-2212. This is a sign of a narrow distribution. The various averages can vary significantly for wider distributions. Thus, for a sample of Al_2O_3-117nfs, characterized by the widest distribution, the arithmetic average size and averaged size by scattering differ by about a factor of 4.

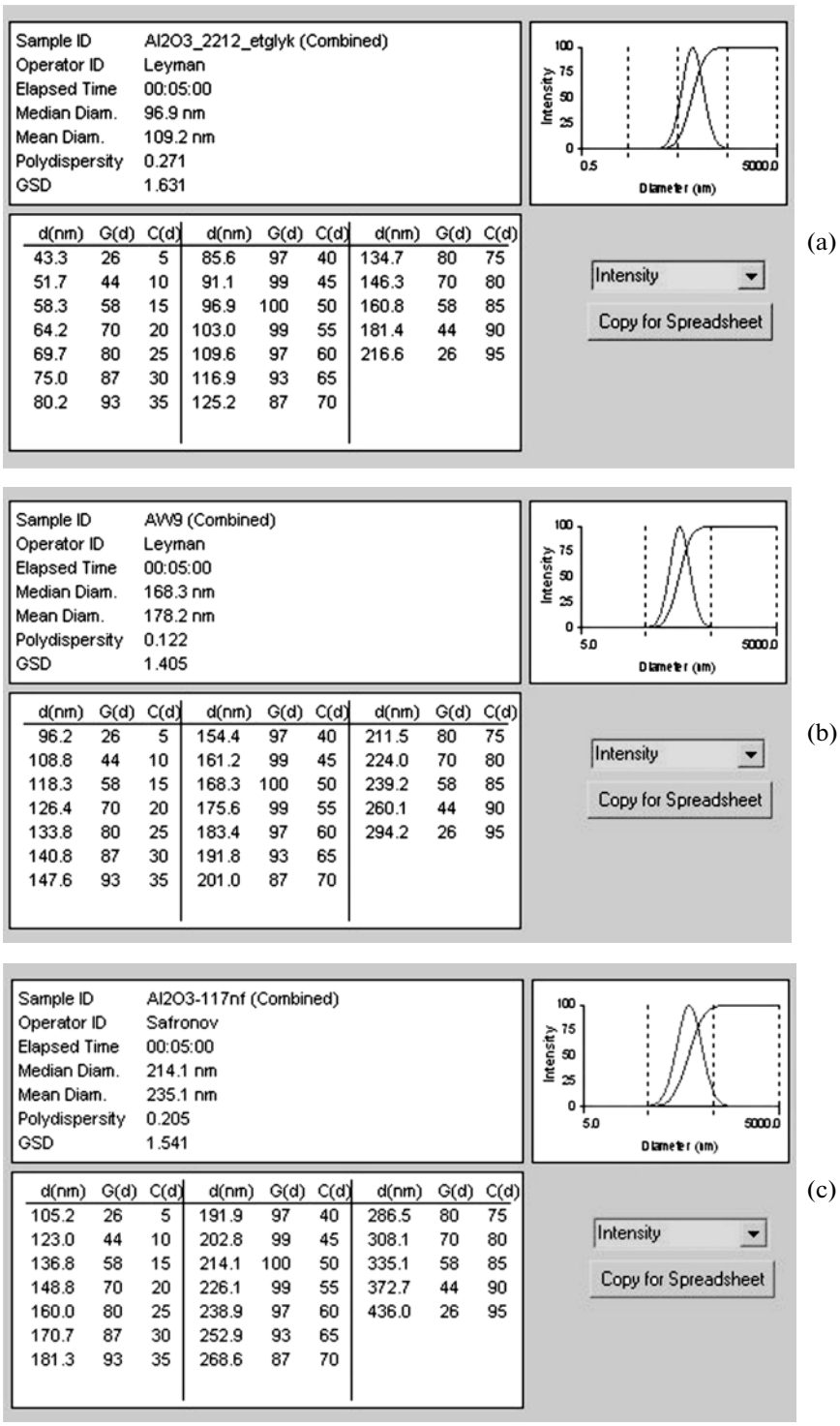
The last column of Table 2 shows the average size of particles calculated from the specific surface area of spherical particles [4]:

$$d_{BET} = \frac{6}{\rho S_{sp}},$$

where S_{sp} is specific surface of the powder and ρ is the density of material.

Table 3. Comparison of dispersion characteristics in dry state and in aqueous suspension

No.	Identification number	d_{sc}, nm		σ	
		In powder	In suspension	In powder	In suspension
1	Al_2O_3-2212	17.4	109	0.391	0.489
2	Al_2O_3-140ns	84.6	178	0.660	0.340
3	Al_2O_3-117nfs	144	235	0.736	0.432



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
43.3	26	5	85.6	97	40	134.7	80	75
51.7	44	10	91.1	99	45	146.3	70	80
58.3	58	15	96.9	100	50	160.8	58	85
64.2	70	20	103.0	99	55	181.4	44	90
69.7	80	25	109.6	97	60	216.6	26	95
75.0	87	30	116.9	93	65			
80.2	93	35	125.2	87	70			

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
96.2	26	5	154.4	97	40	211.5	80	75
108.8	44	10	161.2	99	45	224.0	70	80
118.3	58	15	168.3	100	50	239.2	58	85
126.4	70	20	175.6	99	55	260.1	44	90
133.8	80	25	183.4	97	60	294.2	26	95
140.8	87	30	191.8	93	65			
147.6	93	35	201.0	87	70			

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
105.2	26	5	191.9	97	40	286.5	80	75
123.0	44	10	202.8	99	45	308.1	70	80
136.8	58	15	214.1	100	50	335.1	58	85
148.8	70	20	226.1	99	55	372.7	44	90
160.0	80	25	238.9	97	60	436.0	26	95
170.7	87	30	252.9	93	65			
181.3	93	35	268.6	87	70			

Fig. 3. Unimodal particle distribution by scattering intensity in nanopowder aqueous suspensions: (a) Al_2O_3 2212, (b) Al_2O_3 140ns, and (c) Al_2O_3 117nfs.

The DLS method was used to identify particle sizes and the distribution of the particle sizes in aqueous suspensions of Al_2O_3 nanopowders. Al_2O_3 nanopowders in water form stable suspensions in the absence of special stabilizers. This is a consequence of self-stabilization of nanopowders suspensions obtained by EEW and LEC methods [5].

Unimodal particle distributions by intensity of scattering in aqueous suspensions for the investigated nanopowders are shown in Fig. 3.

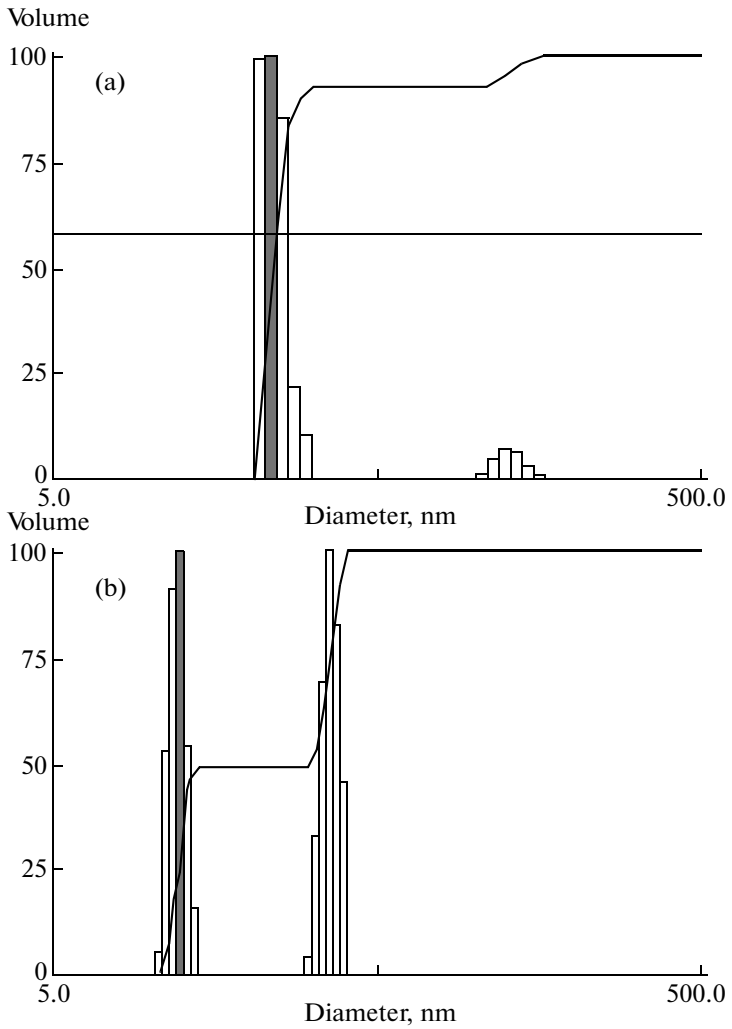


Fig. 4. Curves of weighted bimodal distribution obtained by DLS for aqueous suspensions of nanopowders: (a) Al_2O_3-2212 and (b) Al_2O_3-117nfs.

The distributions, which are shown in Fig. 3, characterize not the number of particles of a specific size but the relative intensity of scattering from the particle fraction of a specific size, so they cannot be directly compared with the distributions in the dry state. A comparison can be made using the values of the mean value d_{sc} and variance of the distribution, which does not depend on the method of averaging. The values of average particle size and dispersion of the log-normal distribution are shown in Table 3.

It can be seen from Table 3 that the particle size in the suspension is several times greater than the size of particles in the dry powder. These differences are greatly increased for superfine powder Al_2O_3-2212. These differences clearly indicate the aggregation of the nanoparticles in aqueous suspension.

A multimodal distribution based on the DLS data was built for all suspensions. In all cases it was the same type and was characterized by the presence of two fractions. Figure 4 shows examples of weighted multimodal distribution obtained for samples Al_2O_3-2212 and Al_2O_3-117nfs. The figure shows that the size of the first fraction is close to the value d_w defined by curves of particle size distribution in the dry powder (Table 2). This indicates that isolated nanoparticles are present in the suspension in a sufficient amount. However, along with these particles there is a significant part of aggregates in the suspension corresponding to a second maximum at a bimodal distribution curve.

According to the DLS weight, the proportion of individual particles of Al_2O_3 in the suspensions is 40–

Table 4. Particle size in Al_2O_3-140ns suspension

	Average intensity	Average wt.	Average number	GSD
TEM (2027 particles)	70.5	42.4	19.4	1.703
DLS (Brookhaven)	70.4	52.8	37.8	1.432

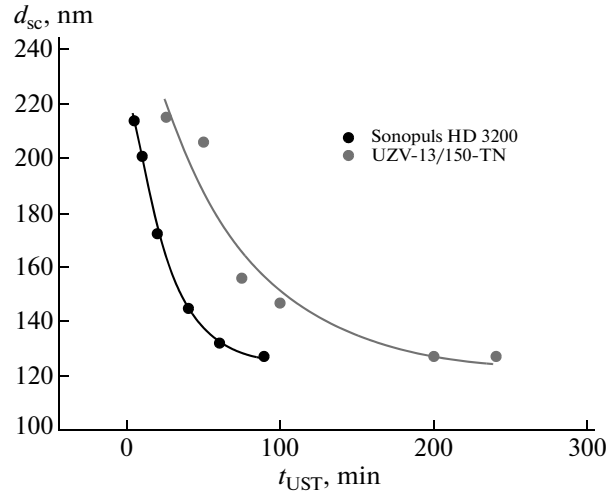


Fig. 5. The dependence of the hydrodynamic diameter of the aggregates of time and type of continuous ultrasonic treatment for Al_2O_3-140ns suspension stabilized using 5 mM sodium citrate solution.

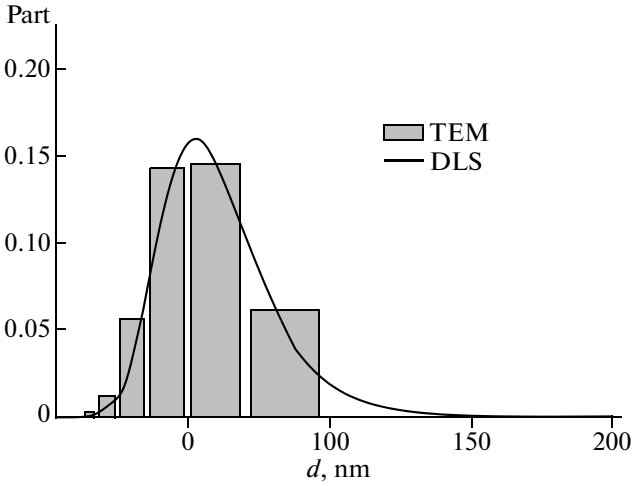


Fig. 6. Size distribution of particles in Al_2O_3-140ns suspension by intensity of light scattering.

80% depending on the degree of dispersion of the source nanopowder; the remainder are aggregates, the size of which is approximately three times higher than the size of individual particles [1]. At the same time, the results show that additional disaggregation is needed for suspensions containing only individual particles.

The ultrasonic treatment of a suspension is a standard methodological procedure of its preparation. UST efficiency for suspensions of nanoparticles was investigated in the literature [6, 7]. The result of these and other studies is the conclusion that the UST method cannot fully disaggregate nanoparticles which are present in the suspension. However, in spite of the commonality of this conclusion, the specific values of the degree of disaggregation upon UST using different sources vary very much. Therefore, the effect of UST on the degree of aggregation of the particles in suspension for the investigated suspensions has been studied.

One limiting point of using UST to disperse the nanopowders in a liquid medium is the heating of the suspension during the process that does not allow performing it long enough. Using high-power ultrasonic emitters for 3–5 minutes of suspension treatment at a power of 100–300 watts is sufficient to render the suspension heated to boiling. Raising the temperature generally adversely affects the stability of aqueous suspensions. [4] Therefore, it is necessary to cool the suspension during UST. Both of these approaches have been tested for investigated suspensions.

Suspensions of alumina nanopowders were prepared by dispersal in distilled water with the addition of sodium citrate stabilizer by means of a Sonopuls HD 3200 submersible ultrasonic disperser (power 160 W) and a UZV-13/150-TN ultrasonic bath (power 240 W).

Figure 5 shows the mean hydrodynamic size of the d_{sc} aggregates for suspension Al_2O_3-140ns with a concentration of 10 g/L electrostatically stabilized by a 5 mM solution of sodium citrate depending of the processing time and the type of dispersant with a continuous cooling of the suspension.

It is seen that aggregate size of Al_2O_3-140ns naturally decreases, reaching saturation during UST. The minimum size (127 nm) is reached after 1.5–4 h of treatment depending on the type of dispersant. This value can be considered the limit of the nanoparticle disaggregation of the Al_2O_3-140ns powder upon UST. This value differs quite substantially from d_{sc} for this sample, calculated from the particle size distribution in the dry powder (Table 2), which is 85 nm. Therefore, UST does not allow particles to disaggregate completely; however, the hydrodynamic size of the aggregates during UST is greatly reduced.

Undestroyed aggregates present in the suspension may be separated by centrifugation. Centrifugation was performed for 5 min at 10000 rev/min. The centrifugal acceleration was 18000 g. Figure 6 shows the distribution of particles in Al_2O_3-140ns aqueous suspensions by scattering intensity after centrifugation. The average d_{sc} values in the Al_2O_3-140ns suspension after UST and centrifugation according to TEM and DLS are shown in Table 4.

It is seen from Fig. 6 and Table 4 that, when comparing the particle size distributions obtained by the intensity of light scattering in DLS and TEM techniques, there are no units and only individual particles are present in the separated suspension. Thus, it has been shown to be fundamentally possible to obtain disaggregated aqueous suspensions of nanoparticles of alumina obtained by high-performance high-energy physical dispersion methods and the technique to do so is illustrated. The absence of aggregates allows

us to obtain suspensions with a narrow particle size distribution.

CONCLUSIONS

Al_2O_3 nanopowders taken for research obtained by the electrical explosion of wire and laser evaporation and condensation according TEM data consisted of nonagglomerated spherical particles with a lognormal size distribution. Nanopowders have a wide range of dispersion with a specific surface area of from 20 to 140 m^2/g, allowing us to characterize the specificity of disaggregation. According DLS, stable aqueous suspensions of nanoparticles stabilized by sodium citrate with a concentration of 5 mM contain a significant part of aggregates. It is shown that the aggregates in the suspension are in "equilibrium" with the individual nanoparticles. Primary aggregates are found in suspension, presumably initially present in the air-dry powder. Ultrasonic treatment is an effective method of nanopowder disaggregation in aqueous suspension. The dynamics of the average particle size for the continuous ultrasonic treatment of suspension concentration of 10 g/L for 1.5–4 h for two types of dispersing devices has been investigated. It was shown that the average size of the aggregates in suspension decreases exponentially 1.5–2 times, and the part of individual particles increases significantly from 45 to 85%. The following centrifugation of suspension at 18000 g makes it possible to separate the undestroyed aggregates and obtain suspensions of Al_2O_3 individual particles in which the size distribution obtained by DLS and TEM coincide within experimental error.

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